SUPPORTING INFORMATION

Spectroscopic Studies of the Modification of Crystalline Si(111) Surfaces with Covalently-Attached Alkyl Chains Using a Chlorination/Alkylation Method

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Surface Characterization by X-ray Photoelectron Spectroscopy

The XPS chamber was maintained at a base pressure of less than $2x10^{-10}$ torr. During data collection, the pressure was higher than this base pressure but was always less than $2x10^{-8}$ torr. The XP spectrometer was pumped by a CTI Cryogenics-8 cryopump and was attached via gate valves to other custom-built chambers that housed the quadrupole mass spectrometer and other surface science instrumentation. These other chambers were also pumped by CTI Cryogenics cryopumps. Samples could be introduced into these chambers through two load locks that were connected through gate valves and were pumped by turbomolecular pumps (Varian models V80 and V200) that were backed by mechanical pumps (Varian model SD-300). These two load locks were always backfilled with O_2(g)-free N_2(g) and could be taken from atmospheric pressure to approximately 10^{-7} torr in ≈10 min. One load lock opened to atmosphere and facilitated introduction of samples from air into the UHV system. The other load lock opened through a gate valve into a custom-built glove box that was continuously purged with oxygen-free N_2(g).

Samples prepared in the inert atmosphere of the N_2(g)-purged glove box could be introduced directly into the UHV system through this load lock without exposure to air. The silicon samples were mounted on custom-made stainless steel or aluminum stubs using gold-plated molybdenum clips or gold-plated screws which also served to ground the samples.

A typical XPS measurement of a surface consisted of one survey scan from 0-700 BeV (binding eV) binding energy followed by a high resolution scan of the Si 2p region (98.6-105.4 eV binding energy). Additionally, high resolution scans of the Cl 2p (197.4-204.2 BeV), F 1s (685.9-692.7 BeV) and/or C 1s (282.2-289.0 BeV) regions were also collected as necessary.

Peak fitting routines provided by the M-Probe package software (version 3.4) were routinely used to analyze the data. Peak areas in the survey scan were calculated by the software after a straight line background subtraction and were normalized for the number of scans and collection time per channel. The high resolution scans for the Si 2p, C 1s, F 1s and Cl 2p regions were smoothed by a 3-point smoothing routine before measuring the area under the curve using a Shirley background subtraction.

The substrate-overlayer model used to calculate coverages model assumes that the chlorine, fluorine or alkyl groups are closest to the silicon substrate and that an adventitious hydrocarbon layer is on top of the halogen or alkyl overlayer. To calculate the elemental surface coverage, the peak areas for the elements of concern in the XPS survey scans were ratioed to the area of the Si 2p peak observed in the same survey scan. The thickness of the overlayer was calculated from the relationship:[1]

$$\frac{I_{ov}}{I_{Si}} = \left(\frac{SF_{ov}}{SF_{Si}}\right)\left(\frac{\rho_{ov}}{\rho_{Si}}\right)\left[\frac{1-\exp\left(-\frac{d_{ov}}{\lambda_{ov}\,\mathrm{Sin}\theta}\right)}{\exp\left(-\frac{d_{ov}}{\lambda_{Si}\,\mathrm{Sin}\theta}\right)}\right] \qquad (1)$$

where I_{ov}/I_{Si} is the raw intensity ratio of the overlayer element peak area to the Si 2p peak area, SF_{ov} and SF_{Si} are the modified sensitivity factors for the overlayer atoms and for substrate silicon atoms, respectively, ρ_{ov} and ρ_{Si} are the atomic densities of relevant atoms in the overlayer and of the substrate silicon, respectively, d_{ov} is the overlayer thickness, λ_{ov} and λ_{sub} are the escape depths for the relevant electrons originating from overlayer and substrate, respectively, and passing through the overlayer, and θ is the take-off angle from the horizontal used in collection of the XPS data.

Elemental sensitivity values were calculated from equation (2), which was provided in the M-probe package software version 3.4:

$$SF_{mod} = SF_{Scof}\left[\frac{1486-BE}{1486-284}\right]^{S_{exp}} \qquad (2)$$

In this equation, SF_{scof} is the unmodified Scofield factor and S_{exp} is the sensitivity exponent, which was 0.65 for the survey scan and 0.60 for the high resolution scans. 1486 (eV) was the energy of the monochromatic K_α line from the Al target and 284 (eV) was the binding energy of the C 1s peak. In this study, all sensitivity factors and peak positions were normalized to the C 1s peak, which was assumed to have a sensitivity factor of 1.00 and a peak position of 284.6 eV binding energy.

(1) Seah, M. P. Quantification of AES and XPS. In *Practical Surface Analysis*; 2nd ed.; Briggs, D., Seah, M. P., Eds.; John Wiley & Sons: Chichester, 1990; Vol. 1; pp 201-255.

Figure S-1. X-ray photoelectron survey spectra of a (111)-oriented Si surface after exposure to (a) 5:1 NH_4(aq)/HF(aq) to produce Si-H termination, (b) chlorination with PCl_5, and (c) alkylation with $C_6H_{13}Li$.

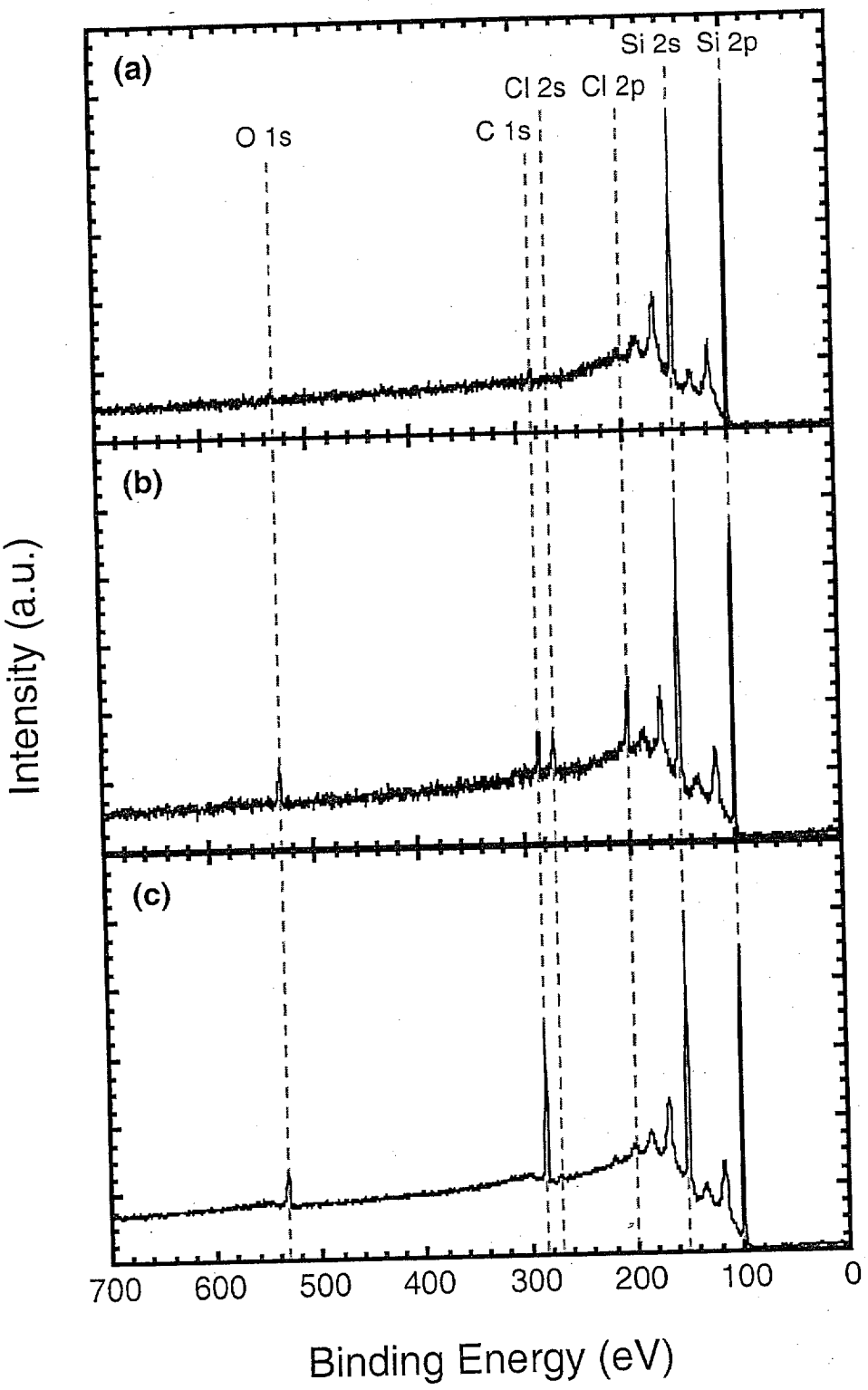
Figure S-2. S- and p-polarized infrared absorption spectra for H-terminated Si surfaces collected in (a) glancing transmission (TIR) mode and (b) attenuated total multiple internal reflection (ATR) mode. Transmission IR spectra were collected on oxidized silicon samples which were then used as background, and the same surfaces were etched in 5:1 NH_4F(aq)/HF(aq) and 40% NH_4F(aq) to obtain the H-terminated surface.

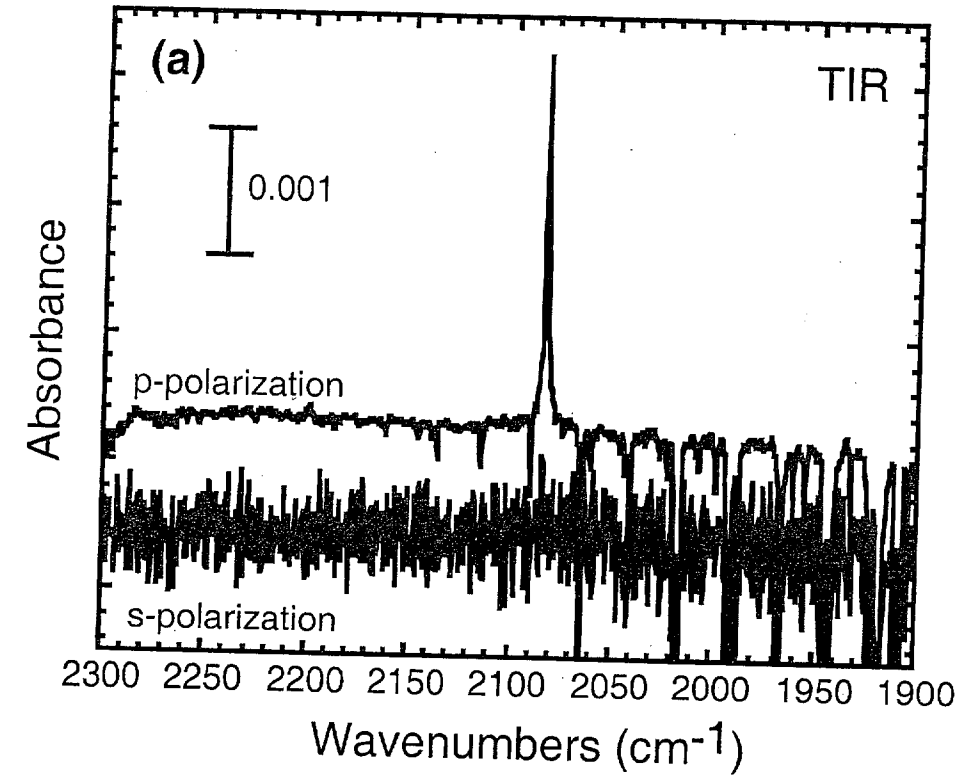
Figure S-3. Auger electron spectra of a chlorine-terminated Si surface before (thin solid line) and after (thick solid line) thermal desorption. The Cl LMM peak observed at 181 eV disappeared after thermal desorption. Peaks at 92 eV, 272 eV and 503 eV correspond to Si, C and O respectively.

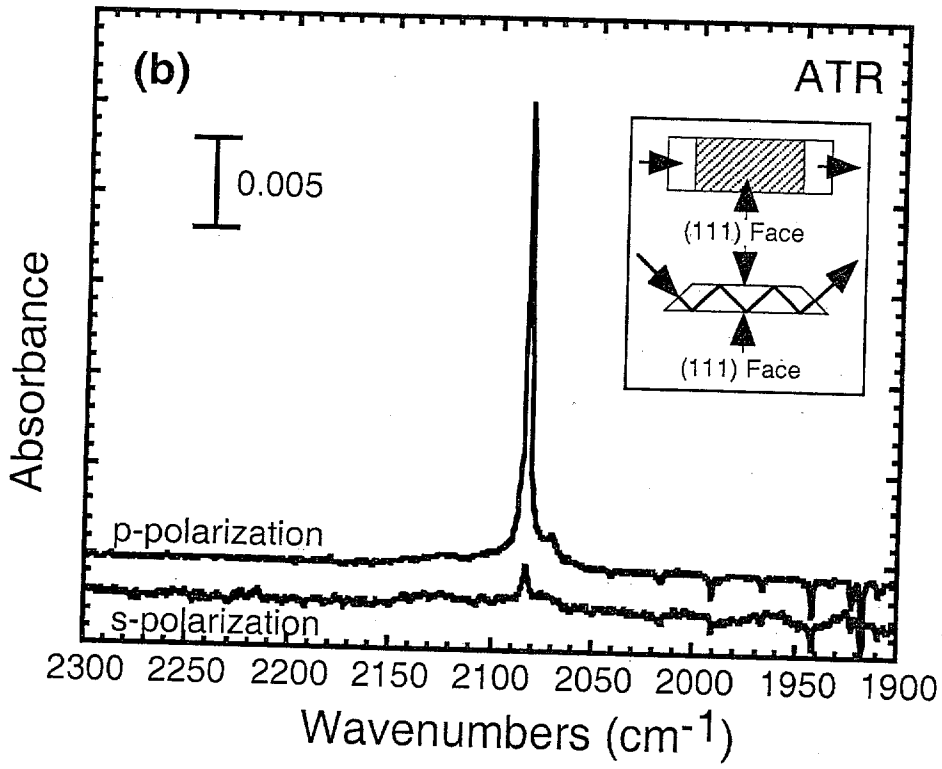
Figure S-4. S- and p-polarized ATR IR spectra of a -$C_{12}H_{25}$ terminated (111)-oriented Si surface formed from exposure of the chlorinated Si surface to $C_{12}H_{25}MgBr$ in (a) the Si-H stretching region and (b) the C-H stretching region. An oxidized silicon surface was used as the background for the spectra in (a) whereas a H-terminated Si surface was used as the background for the spectra in (b). The peak position of the C-H asymmetric stretching peak ($\nu_a(CH_2)$ = 2922 cm^{-1}) suggests a semi-amorphous environment for the alkyl chains. No signal was seen between 3300-3700 cm^{-1} for the alkylated surface, indicating absence of physisorbed or chemisorbed water or -OH groups, within our detection limit.

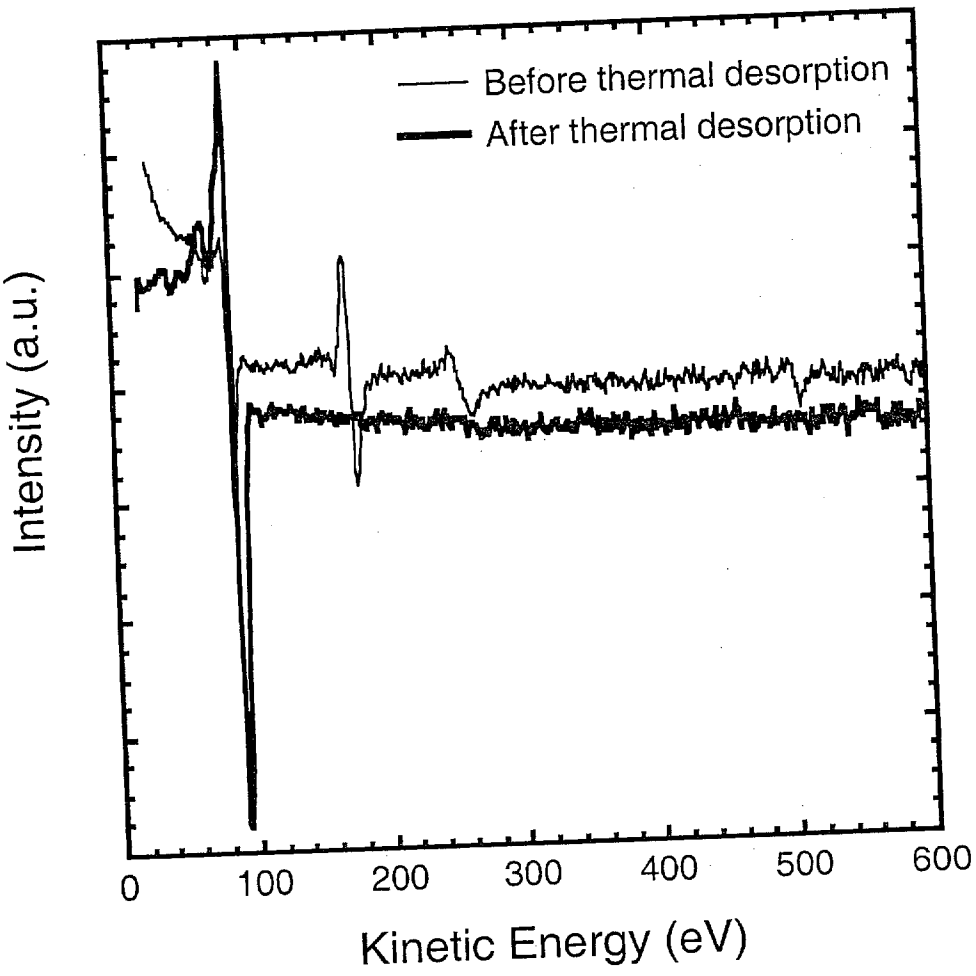
Figure S-5. Auger electron spectra of an ethyl-terminated Si surface (made from exposing the chlorinated Si surface to C_2H_5MgBr) before (thin solid line) and after (thick solid line) thermal desorption. The peaks at 92 eV and 272 eV correspond to Si and C, respectively. A trace amount of Cl is also observed on the alkylated surface, as indicated by a small peak at 181 eV. All peaks except that for bulk silicon disappeared after the sample was heated to ~1200 K and cooled to room

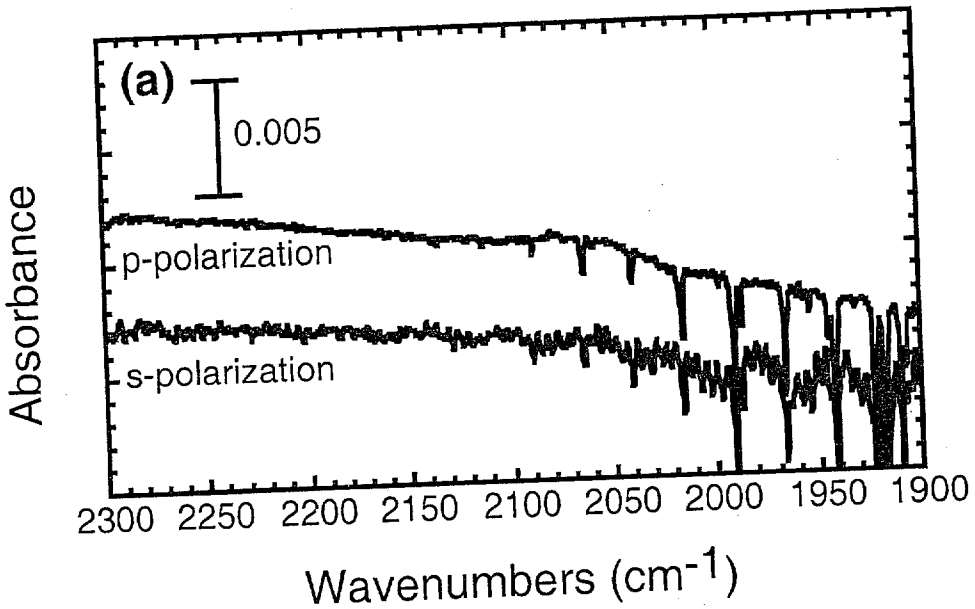
temperature.

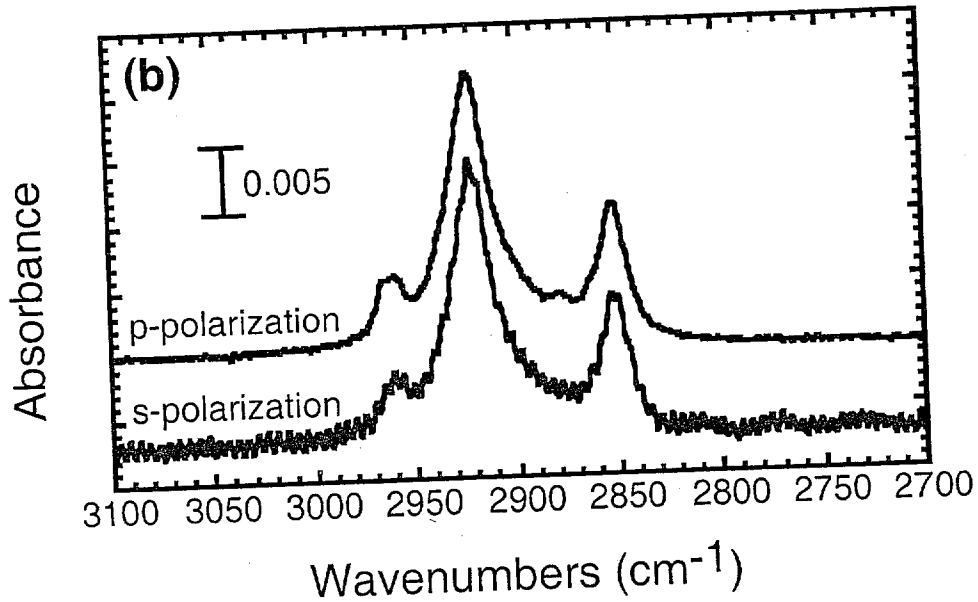

(a)
(b)
(c)
O 1s
C 1s
Cl 2s
Cl 2p
Si 2s
Si 2p
Intensity (a.u.)
700
600
500
400
300
200
100
0
Binding Energy (eV)

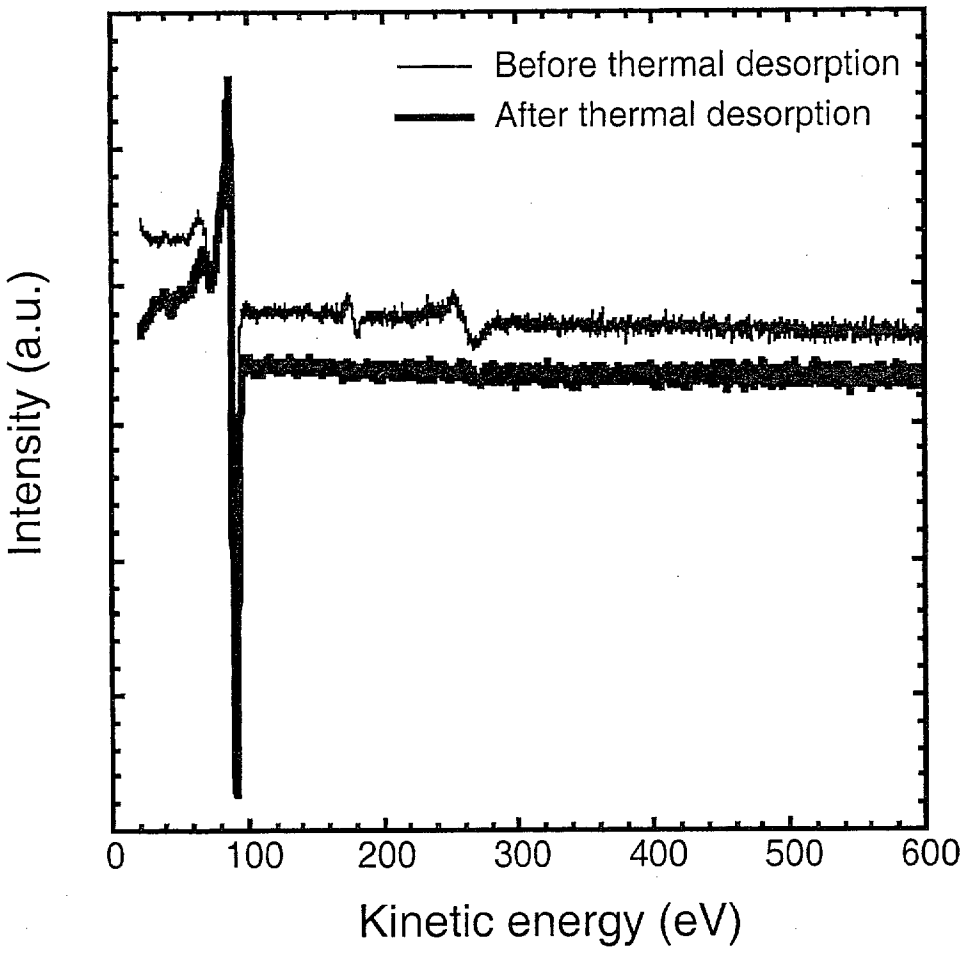

(a)
TIR
0.001
p-polarization
s-polarization
Absorbance
2300 2250 2200 2150 2100 2050 2000 1950 1900
Wavenumbers (cm-1)


(b)
ATR
0.005
(111) Face
(111) Face
p-polarization
s-polarization
Absorbance
2300 2250 2200 2150 2100 2050 2000 1950 1900
Wavenumbers (cm-1)


Before thermal desorption
After thermal desorption
Intensity (a.u.)
0
100
200
300
400
500
600
Kinetic Energy (eV)


(a)
0.005
p-polarization
s-polarization
Absorbance
2300 2250 2200 2150 2100 2050 2000 1950 1900
Wavenumbers (cm-1)


(b)
0.005
p-polarization
s-polarization
Absorbance
3100 3050 3000 2950 2900 2850 2800 2750 2700
Wavenumbers (cm-1)


Before thermal desorption
After thermal desorption
Intensity (a.u.)
0
100
200
300
400
500
600
Kinetic energy (eV)